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Structure property relationship among novel dental composite matrix resins

H. K. SHOBHA*, M. SANKARAPANDIAN*, S. KALACHANDRA*‡, D. F. TAYLOR‡ and J. E. MCGRATH*
** Virginia Tech, Blacksburg, Virginia, 24061-0212, USA*
‡ University of North Carolina, Chapel Hill, North Carolina, 27599, USA

Several novel dimethacrylate monomers of propoxylated diphenols have been synthesized to establish a correlation between their structure and the important properties of viscosity, curing shrinkage and wetting behaviour. These dimethacrylates were designed to possess linear and flexed structures. These new monomers exhibited very much lower viscosities compared to the conventionally used Bis-GMA. Good correlations were obtained for variations of the monomer structures with bulk viscosities and curing shrinkages. However, the wetting behaviour of these resins did not show any trend.

1. Introduction

Requirements for dimethacrylate monomers used in dental composite matrix resins are low curing shrinkage, water sorption and viscosity [1]. In current dental composites Bis-GMA has generally been employed as the matrix resin, but due to its high viscosity (~1200 Pa s) it is normally diluted with more-fluid difunctional monomers. The added diluent monomers tend to adversely affect the properties of the matrix material, increasing water sorption and curing shrinkages [2, 3]. In order to find an improved monomer system for dental restorative resins, several dimethacrylate monomers have been investigated [4–12]. However, there are many difficulties in the design of a monomer structure and the development of an improved monomer system, since the relationship between chemical structure and properties is not well understood.

In order to have a better understanding of the structure–property relationship, a study was undertaken to establish a correlation between monomer structure and properties. To do so, several new monomers have been designed and synthesized. The earlier part of this study dealt with compositional modifications to the core region and side chain structures of Bis-GMA [10].

The research reported here has investigated the effects of variation in molecular shape and conformation on the properties of monomers of fixed composition. Two series of monomers were prepared with compositional similarities to the methyl-substituted Bis-GMA analogue previously investigated [10] (monomer II, Table I). Within each series, molecular structure was varied to produce differing degrees of molecular flexure. The structures of these monomers are shown in Table I. All monomers have the same side chain. Monomers III and IV have bicyclic cores corresponding to monomer II without the central isopropylidene group. Monomers V, VI and VII have only a monocyclic core with the side chains in different relative positions.

The general formula of these monomers is:

$$R–(C_6H_4)x–R$$

where R is $H_2C{=}C(CH_3)–COOCH_2CH(CH_3)O$ and x is 1, 2. The viscosity, curing shrinkage and wetting behaviour of these monomers have been studied and compared with those of Bis-GMA.

2. Experimental procedures

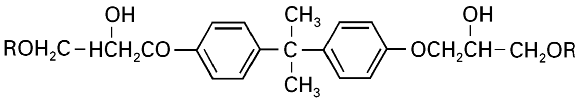
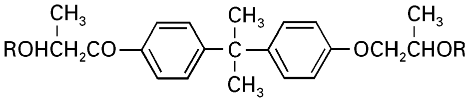
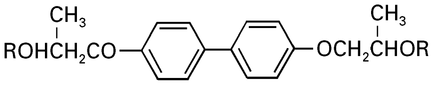
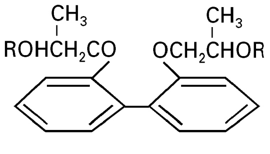
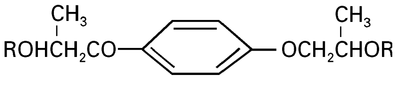
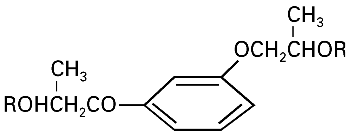
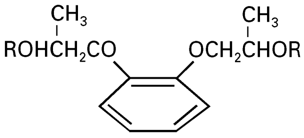
2.1. Materials and methods

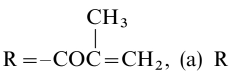
All the phenols used in this study were obtained from Aldrich. Propylene oxide (Aldrich), methacryloyl chloride (Aldrich) and triethylamine (Fisher) were used as received. Tetrahydrofuran (THF) (Fisher) was distilled over CaH_2 before use.

2.2. Characterization

Proton NMR characterization was performed on a Varian Unity 400 (400 MHz) in deuterochloroform solvent in order to confirm the molecular structure and purity. FTIR spectra (Nicolet) of the purified monomers were recorded using NaCl windows. Viscosity measurements were determined with a Brookfield cone and plate viscometer. Densities of the monomers were determined pycnometrically, and polymer densities were measured by hydrostatic weighing. The density difference between the polymer and the monomer was used to calculate curing shrinkage. Contact angle measurements were made using a Rome–Hart contact angle goniometer (Model 100-00) for each of these monomers when applied to dentin, enamel, PMMA and glass surfaces.

TABLE I Bulk viscosities and curing shrinkages of the experimental monomers

	Monomer	Viscosity (Pa s)	Shrinkage (%)
I		1200	6.4
II		0.321	7.5
III		5.71	4.1
IV		0.324	7.7
V		1.85	5.2
VI		1.14	5.8
VII		0.105	7.4



$R = -COC(CH_3){=}CH_2$, (a) References 2, 12

2.3. Preparation of the monomers

All the monomers were prepared by following the general procedure of propoxylation of the diphenol followed by methacrylation.

2.3.1. Propoxylation of the diphenol

The diphenol (0.1 mol) was dissolved in 400 ml THF into which 0.04 mol NaOH dissolved in 10 ml of water was added. 0.4 mol of propylene oxide was added to this mixture, which was then stirred at 45 °C for 24 h. The solvent was then evaporated under reduced pressure, leaving solid products. The solid product was washed several times with hot water. It was then dissolved in chloroform and washed several times with dilute sodium hydroxide solution followed by saturated sodium chloride solution. The organic layer was separated, dried by incorporation of anhydrous $MgSO_4$, filtered and the chloroform was evaporated. The yields were between 80 and 90%.

2.3.2. Methacrylation of the propoxylated diphenols

To 0.05 mol of propoxylated diphenols (as prepared above) dissolved in 300 ml of THF, 0.2 mol of triethyl amine was added and the mixture was cooled to between 0 and 5 °C. Methacryloyl chloride (0.15 mol) was added dropwise with stirring at this temperature, and the temperature was allowed to rise to room temperature after the addition was completed. Stirring was continued overnight and the mixture was filtered to remove the amine-acid salt. After the evaporation of THF under reduced pressure, the resulting viscous liquid was dissolved in ether and the solution was washed several times with dilute HCl, dilute sodium bicarbonate solution and then with saturated sodium chloride solutions. Finally, the organic layer was separated and dried with anhydrous $MgSO_4$, and filtered. 0.05 mol % of 2,6-di-t-butyl-4-methyl-phenol was added as an inhibitor and ether was evaporated under reduced pressure. The yields were found to be more than 90%. The products were analysed by ^1H nuclear magnetic resonance (NMR) and Fourier transform infrared spectroscopy (FTIR).

The proton NMR (in $CDCl_3$ solvent) of these dimethacrylates exhibited simple or complex patterns in the aromatic region (6.7–7.5 ppm) depending on the diphenol used. All the dimethacrylates exhibited the following common peaks: 6.2 ppm (2H, s, vinyl proton *trans* to ester), 5.7 ppm (2H, s, vinyl proton *cis* to ester), 5.2–5.4 ppm (2H, multiplet, methine proton), 3.7–4.1 ppm (4H, multiplet, methylene protons),

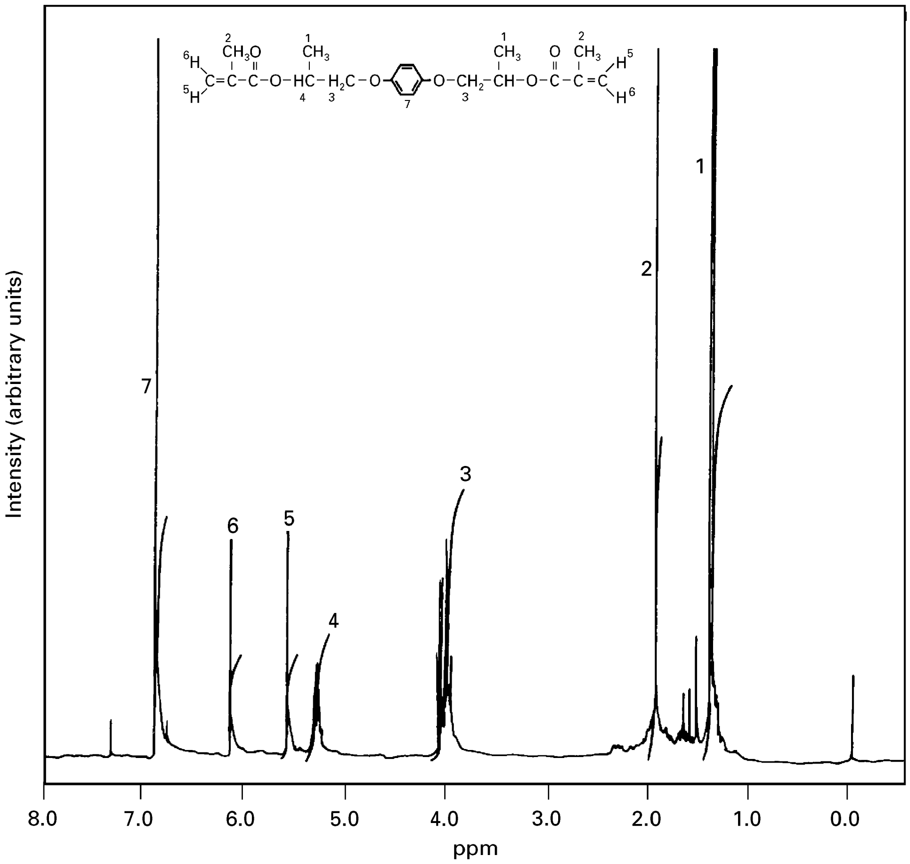


Figure 1 ^{1}H NMR spectrum for 1,4-phenyl propoxylated dimethacrylate.

1.8 ppm (6H, s, methyl protons of the methacrylate group) and 1.25 ppm (6H, d, methyl protons of the propoxyl group). The IR spectra of these dimethacrylates exhibited peaks at 1700–1730 cm^{-1} (carbonyl stretching) and 1630–1640 cm^{-1} (C=C stretching). A typical ^{1}H NMR spectrum for 1,4 diphenyl monomer is shown in Fig. 1.

2.4. Polymerization

A 10 ml sample of each monomer was polymerized in a nitrogen atmosphere using 1 mol % AIBN as free radical initiator. Each polymerization was conducted in a 15 ml test tube sealed with a rubber septum at 80 °C for 10 h, followed by 110 °C for 4 h.

3. Results and discussion

3.1. Viscosity behaviour

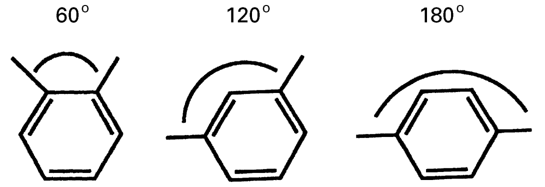
The values of bulk viscosities and the curing shrinkages of the monomers are provided in Table I and the values are compared with those of Bis-GMA.

A careful analysis of the viscosity values in Table I reveals the following:

(i) The very high viscosity of Bis-GMA may be attributed to the intermolecular hydrogen bonding. All the experimental monomers investigated exhibited much lower viscosities compared to Bis-GMA due to the absence of hydrogen bonding in these systems as a result of the –CH_3 substitution for the –OH group. (ii) Comparison of the viscosities among these monomers reveals that the structural variation of these core ring structures profoundly affects the viscosity behaviour of these monomers. The flexed monomers (1,2-phenyl and 2,2′-biphenyl) exhibited the lowest viscosities, while their linear analogues (1,4-phenyl and 4,4′-diphenyl) exhibited high viscosities. The low viscosities of the flexed monomers may be related to free volume effects [13]. Flexed monomers possess larger free volumes and exhibit low viscosities while the free volumes of the linear analogues are less, and hence they exhibit high viscosities. (iii) Comparison of the 1,4-phenyl (monomer V) and 4,4-diphenyl monomers (monomers III) suggests that incorporation of an additional phenyl ring in the dimethacrylate increases rigidity and hence produces higher viscosity in the latter system. (iv) However, incorporation of the isopropylidene units between the biphenyl units (Bis-A CH_3) results in the disruption of the rigidity and hence the viscosity drops off drastically.

3.2. Curing shrinkages

The values of curing shrinkages of the experimental monomers are shown in Table I. In general, monomers with low viscosities exhibited high curing shrinkages. Detailed comparison of the viscosity and cure shrinkages of the 1,2-, 1,3-, and 1-4-phenyl dimethacrylates (monomers V, VI and VII) has been attempted. Considering the angle between the dimethacrylate units on the phenyl rings in these systems as shown below,



the variation of the curing shrinkages and viscosities with this angle is shown in Fig. 2. It is apparent from Fig. 2 that viscosity and curing shrinkage behaviours follow exactly reverse trends. This behaviour may be explained as follows. As mentioned earlier, the high viscosities of the linear monomers (III and V) is the result of possible low free volumes due to the efficient packing. In contrast, flexed monomers (IV and VII) are expected to possess larger free volumes, and on curing they exhibit large shrinkages. The monomer and polymer densities and curing shrinkages for the monocyclic monomers (V, VI and VII) as a function of the angle between the methacrylate groups are given in Table II and Fig. 3. There is a clear increase in monomer density (and implicit decrease in the

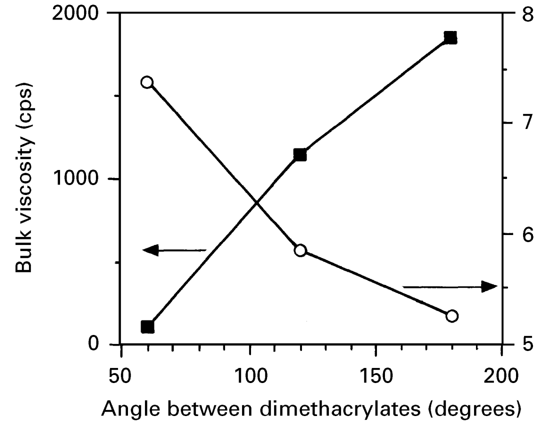
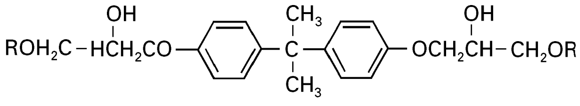
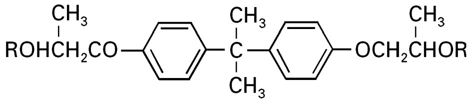
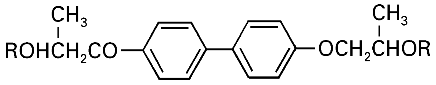
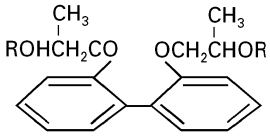
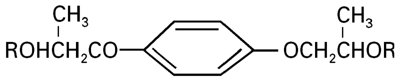
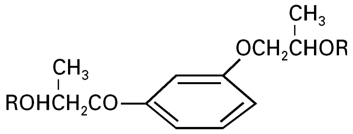
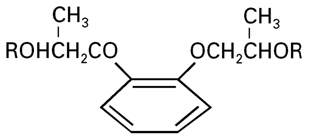


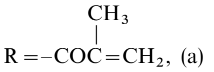
Figure 2 Variation of the bulk viscosity (■) and percentage cure shrinkage (○) with the angles between the subtituents in the phenyl ring.

TABLE II Densities and curing shrinkages for monocyclic monomers

Monomer	Angle	Density (gm/ml)		Shrinkage (%)
		Monomer	Polymer	
VII (ortho)	60°	1.095	1.182	7.37
VI (meta)	120°	1.114	1.183	5.89
V (para)	180°	1.127	1.189	5.24

TABLE III Contact angles of the experimental monomers on different surfaces

	Monomer	Contact angle (degrees)			
		Glass	PMMA	Enamel	Dentin
I		–	–	–	–
II		19	14	11	16
III		19	16	17	17
IV		11	11	10	11
V		10	11	12	12
VI		19	18	12	10
VII		15	12	7	9


$R = -CO\overset{CH_3}{\overset{|}{C}}=CH_2$, (a) References 2, 12

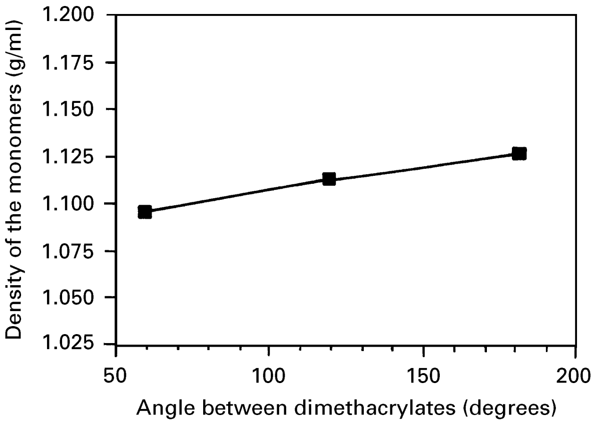


Figure 3 Variation of the density of the monomers with the angles between the substituents in the phenyl ring.

volume) with increasing angle. The polymer densities are nearly uniform with only a slightly higher density in the polymers of the 180° monomer. Thus the difference in curing shrinkage can be attributed almost totally to free volume differences in the monomer.

3.3. Wetting behaviour

The wetting behaviour of these experimental monomers was investigated on different surfaces: glass, PMMA, dentin and enamel. The results are given in Table III. As seen in Table III, all the experimental monomers exhibit good wetting behaviour with these surfaces. However, no correlation between the structure of the monomers and the wetting characteristics could be obtained. This may be explained as follows. Wetting is a result of interaction of these monomers with these surfaces. Since all the experimental monomers investigated possess similar chemical functional groups, it is reasonable that they would interact with the surfaces in a similar way. The additional phenyl rings or the position of the substitutents in these monomers do not seem to play any role in wetting characteristics.

4. Conclusion

Five new experimental dimethacrylate monomers have been designed and synthesized. The structural variations of these monomers correlate well with the viscosity and curing shrinkage behaviour. Generally, flexed monomers exhibit low viscosity and high curing shrinkages compared to their linear analogues. The wetting ability of these monomers is high, but seems to be independent of structural variations.

Acknowledgement

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